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potassium bromide

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# Development of the CN⁻ Solid State Vibrational Laser

## FINAL REPORT

period: August 1, 1985 through October 31, 1988

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# 1. PROJECT SUMMARY

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Our IR pumping experiments have demonstrated for the first time the feasibility of solid state mid-infrared lasers based on purely vibrational transitions of molecular impurities embedded in a host matrice. In the first experiments pulsed oscillation at 2054 $cm^{-1}$ was obtained on the 2 -> 1 transition of $CN^-$ ions in KBr host following pulsed optical pumping of the $CN^-$ lower laser level. Subsequent research then focused on the response of directly pumping the upper vibrational laser level by means of a color center laser tuned to the weakly allowed first overtone transition. For cw pumping, cw lasing was observed. It is the result of the strong lifetime-shortening effect produced by rapid vibration-vibration transfer. In addition, it was discovered that since the upper laser level is fed by this process, an enhancement of the laser efficiency occurs. Still higher concentration $CN^-$ lasers have been studied in two additional series of experiments. By using an open resonator configuration, cw oscillation at 4.9 $\mu m$ has been observed on the 2 -> 1 vibrational transition of $CN^-$ impurities embedded in KI. Population inversion in this device is produced by direct optical pumping of the first overtone transition at 2.42 $\mu m$ with a tunable color center laser. By using a closed resonator, simultaneous pulsed laser output has been observed from the 3 -> 2 and the 2 -> 1 transitions following long pulse pumping of the second overtone transition with the recently developed high power $NaCl:F_2^+:O^{2-}$ color center laser. If other diatomic defects in crystals are found to behave similarly to $CN^-$ then solid state vibrational lasers could be practical for a variety of applications in the IR and FIR spectral regions.

## 2. FINAL REPORT

### 2.1 Introduction

Since Maiman's original invention of the ruby laser in 1960[1], a large variety of fixed frequency and continuously tunable solid-state lasers have been developed. Spanning a frequency region from the visible to the mid-infrared, the gain media of these devices are composed of such diverse materials as impurities of transition metals and rare earth ions in insulators (Nd:YAG[2], alexandrite[3], Ho:CaF$_2$[4], Ce:YLF[5]), color centers in alkali halides[6] and alkaline earth oxides[7], and p-n junctions of binary, ternary, and quaternary compound semiconductors (GaAs[8], AlGaAs[9], PbSnSe[10], InGaPAs[11]). Despite this variety, a universal attribute of these different devices is that the lasing transition occurs exclusively between different electronic states of the laser active constituients. By comparison, not only have analogous electronic state lasers in the gas phase been developed (Ar$^+$[12],Kr$^+$[13], HeNe[14], N$_2$[15]), but also gas lasers based on vibrational (or more properly ro-vibrational) transitions of molecules in their electronic ground states (CO$_2$[16], CO[17], N$_2$O[18], HF[19]).

The explanation for the conspicuous absence from the above list of devices of a solid state laser based on purely vibrational transition is partly historical. Visible, electronic state luminescence in solids and gases has been well studied for decades. Convenient incoherent pumping techniques including electric discharges and UV flashlamps, combined with the photon counting capabilities of photomultiplier tube detectors available in the visible and near infrared regions of the spectrum, have greatly facilitated the investigation and practical application of electronic state transitions. But more fundamentally the principle obstacle to the construction of a solid state vibrational laser has been that extremely low fluorescence quantum efficiencies disadvantageous for laser applications are almost universally observed for vibrational transitions in solids, whereas high quantum efficiencies are commonly observed for their electronic counterparts. Roughly speaking, this circumstance is a

consequence of the larger reduced mass associated with molecular vibrations compared with the electronic mass, which implies lower transition frequencies and weaker radiative transition moments. Consequently, nonradiative decay of, say, an excited impurity state into lattice phonons or excitations of the defect space is expected to be much more likely for a vibrational mode than for an electronic state. Indeed, nonradiative vibrational relaxation times for matrix-isolated molecules typically fall in the nanosecond[20] or perhaps microsecond regime, whereas radiative lifetimes are larger than 1 msec. Direct observations of vibrational fluorescence in the defect solid state are very rare, and in most of these cases, relaxation is still dominated by nonradiative processes[21-25].

Nevertheless, a few examples of vibrational relaxation in solids dominated by radiative transitions have been discovered. Vibrational fluorescence was first observed for CN⁻ by Field and Sherman in 1967[26]. In 1972, a 15 msec fluorescence lifetime was reported[27] for CO molecules embedded in solid Ar and Ne matrices at liquid helium temperatures. These workers naturally recognized the potential application of their discovery to solid state lasers, and in later experiments[28-30] population inversions were readily observed in the argon:CO system. Apparently, however, the engineering difficulties associated with producing large, optical quality inert gas crystals and optical resonators at cryogenic temperatures discouraged further developement. After these ground-breaking experiments, little progress was made throughout the following decade.

In 1983, the CN⁻ fluorescence was rediscovered[31,32] and a fluorescence decay time of 6 msec was measured at 15 K. The obvious great advantages of this ionic system over the van der Waals one are that large, high optical quality alkali halide crystals are easily grown, and can be readily cleaved, polished, and optically coated at room temperature. These advantages have for the first time made feasible a solid state laser[33,34] based on vibrational transitions of matrix-isolated molecules.

Fundamental experimental results have been obtained in the last three years on the

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operating characteristics of prototype KBr:CN-, KI:CN-, and RbI:CN-4.9 μm lasers in a variety of optical resonator configurations and using several optical pumping techniques[35-37]. A great deal of information has been obtained regarding the CW fluorescent properties of these matrix isolated molecules at both high[38] and low temperatures[39]. Finally a new nonresonant method for pumping the vibrational manifold has been discovered and some preliminary time dependent fluorescent studies have been made which show that population inversion can be obtained in this UV-EXCIMER laser pumping mode[40,41]. In all of these fluorescence and laser experiments the influence of highly efficient, vibrational energy exchange processes (V-V transfer) is observed to occur between donor/acceptor pairs of excited CN- ions. Remarkably, these cross-relaxation processes lead to populations in excited vibrational states as high as $v = 26$, and therefore strongly influence the vibrational kinetics[39]. Alhtough V-V transfer has been studied in the AR:CO system[28-30], the new context in solid state laser kinetics for energy transfer processes has led to the observation of unusual solid state laser phenomena, including energy transfer induced cw oscillation. For this reason a dominant theme of the research has been and continues to be focused on the physics of vibrational energy transfer in the alkali halide:CN- system.

## 2.2 Fluorescence Experiments

### 2.2.1 High temperature lifetime measurements

A doubled $CO_2$ laser provides a convenient pump for examining the 0 -> 1 vibrational stretch mode transition of CN- matrix isolated in alkali halide crystals. A representative room temperature laser induced IR emission spectrum for KBr:CN- is shown in Fig. (1a). Except for the scattered light peak at the pump frequency, the spectrum is broad and featureless, and roughly corresponds to the 300 K absorption lineshape observed for the system. Since this fluorescence decay signal is well described by an exponential decay law the relaxation times can be extracted. We find that the CN- vibrational lifetime varies
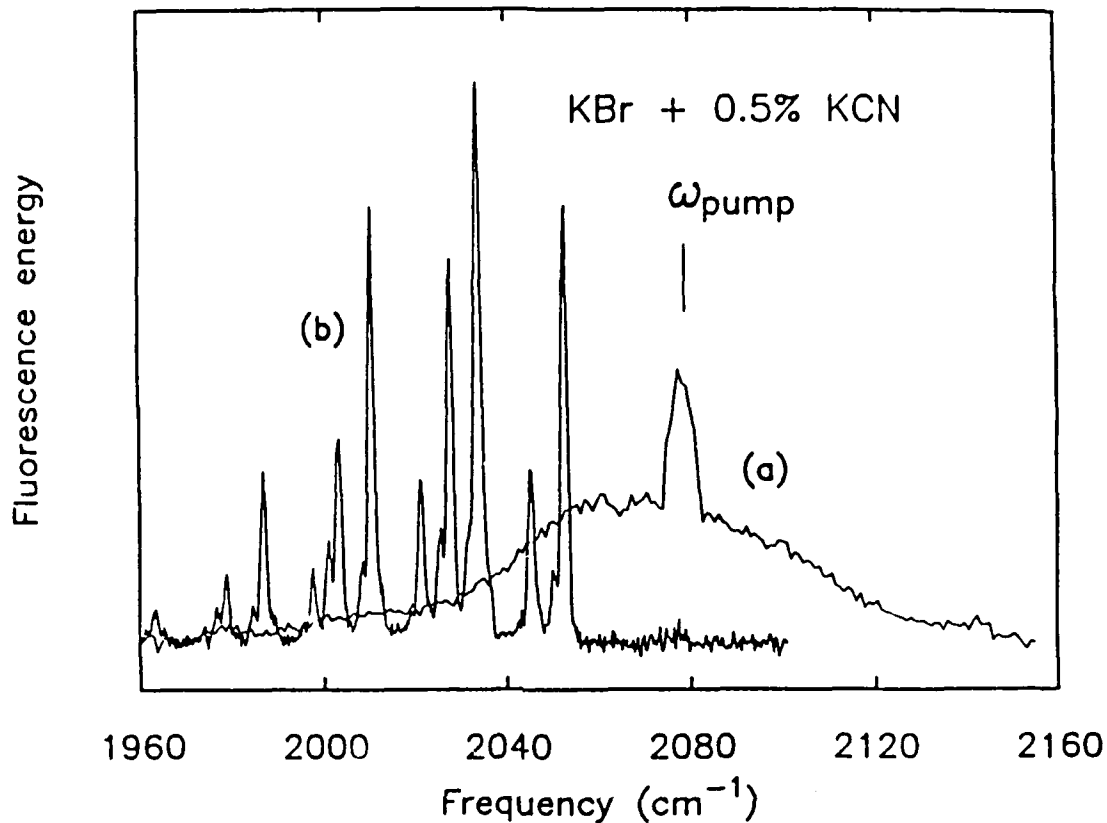
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Figure 1a. Room temperature vibrational fluorescence for KBr + 0.5% KCN. The resolution is 9 cm$^{-1}$, as indicated by the width of the the large scattered light peak at the pump frequency.

Figure 1b. Emission spectrum at 1.7 K. The strongest feature is from the vibrational mode associated with the carbon 13 isotope in natural abundance.

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strongly from host to host[38]. This result can be understood in terms of a high order

multiphonon decay process is expected to provide the nonradiative decay component to the

vibrational decay rate. Thus, those hosts such as CsI or RbI with small Debye

temperatures or optic phonon frequencies should show correspondingly long vibrational

lifetimes. In particular, an energy gap law of the form

$$\tau^{-1} = A\exp(-fN) \qquad (1)$$

relates the the vibrational lifetime to the number of decay phonons N, and to a pair of

constants characteristic of the phonon coupling[20]. Figure (2) shows a semilogarithmic

plot of the observed room temperature lifetimes as a function of the number of longitudinal

optic phonons required to conserve energy. Except for the potassium salts, quite

reasonable agreement with the energy gap law is obtained, as shown by the straight line fit

drawn in the Figure. (The potasium salt discrepancy will be considered again in Sec. 3.4.)

We find that the measured temperature dependence of the relaxation rate is much to slow to

correspond to the multiphonon process and much too fast to be identified with rotational

relaxation[42].

The question of the source of CN⁻ vibrational relaxation at room temperature remains

unresolved. The fact that a reasonably strong temperature dependence is observed for the

fluorescence lifetime, and that reasonable agreement is obtained between the multiphonon

model and the observed temperature dependence for at least a few of the host lattices

suggests that some aspects of the relaxation mechanism should be attributed to a

multiphonon process. It is conceivable that due to the larger rotational potential barriers to

be expected for the alkali halides over those of rare gas solids, librational relaxation might

participate together with multiphonon decay to relax the CN⁻ vibration. In this way fewer

lattice phonons would be required hence a softer temperature dependence would result. At

present there is not enough data to support this or any other hypothesis. It may also be

possible that lattice excitations beyond the harmonic approximation are important. A strong
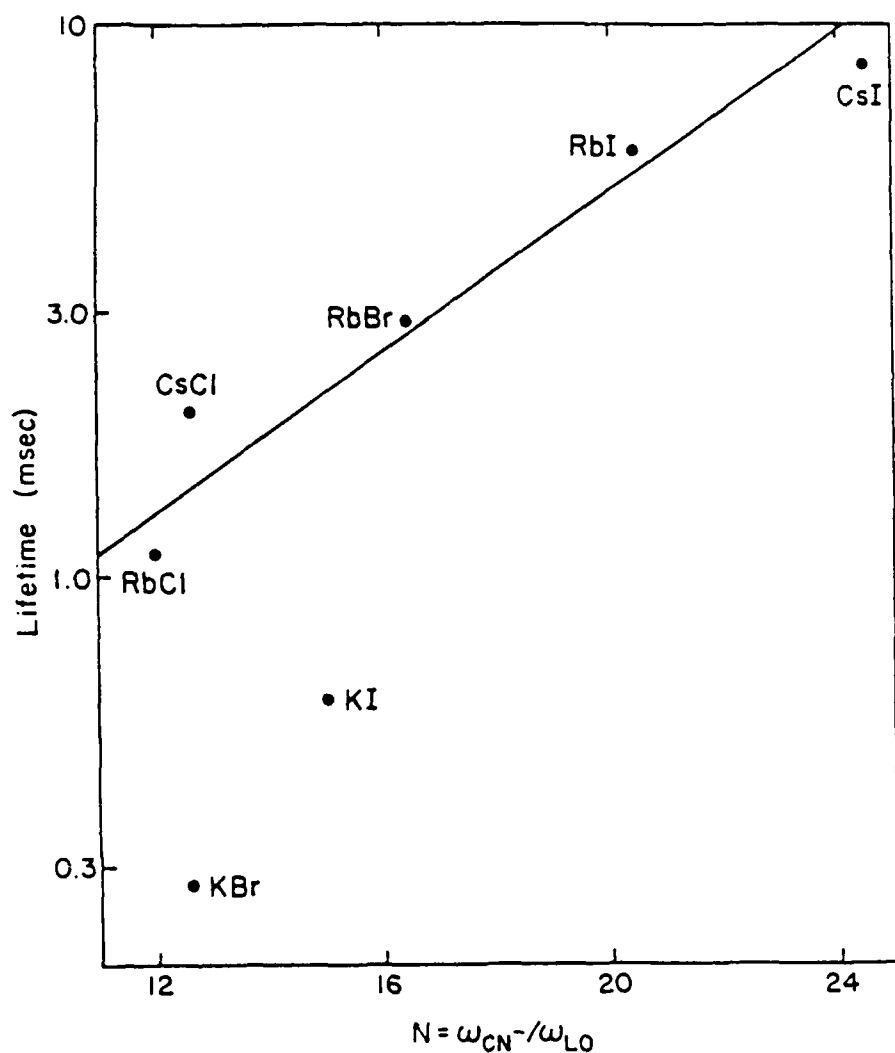
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Figure 2. Semilogarithmic plot of the 297 K fluorescence lifetimes as a
function of the number of longitudinal optic phonons required to relax the
$CN^-$ vibrational mode. Except for the pottasium salts, an energy gap law
is indicated by the straight line fit drawn through the points.

hint that other degrees of freedom may be involved is shown in Fig. (3). The data at 1.7 K does not match up with data taken at higher temperatures on the same crystal. The dashed line shows the interpolated temperature dependence in the unexplored region. A closer look at the fluorescence lifetime between 1.7 K and room temperature is clearly needed to help further decide the number of the degrees of freedom involved in the vibrational relaxation dynamics.

### 2.2.2 Reversible OH⁻ trapping effects

An interesting impurity trapping effect on the fluorescence life time of $CN^-$ was discovered for RbI and RbBr host crystals[38]. During a cycle of the sample temperature from 300 K to 550 K and back to 300 K, larger fluorescence lifetimes were observed on the cooling stage of the cycle. Contined experimentation indicates that the source of this temperature reversible trap is atmospheric water vapor which provides a source of $OH^-$ ions which rapidly diffuse through the RbI and RbBr lattices. Indeed, for a RbI sample exposed to air following a temperature cycle, the large fluorescence lifetimes relax toward their smaller pre-cycle values over a period of days. For a sample maintained in an evacuated chamber at a pressure less than one torr, no decrease in lifetime has been observed over a two week period[42].

That the $OH^-$ ions themselves constitute the trapping center is unlikely due to the large $1200 \, cm^{-1}$ mismatch of the $OH^-$ vibrational frequency above the $CN^-$ frequency. A more likely candidate would be a trapped complex formed by the $OH^-$ ion with another molecular species already present in the crystal. The temperature cycling effect on the fluorescence lifetime would then be understood as the thermal dissociation of the complex.(Sec. 3.4 considers another possibility.) Impurity vibrational trapping effects have been observed in rare gas systems[28]. The new feature introduced in the present high temperature experiments, however, is that the defect chemistry can also be an important factor in determining the vibrational fluorescent lifetime.
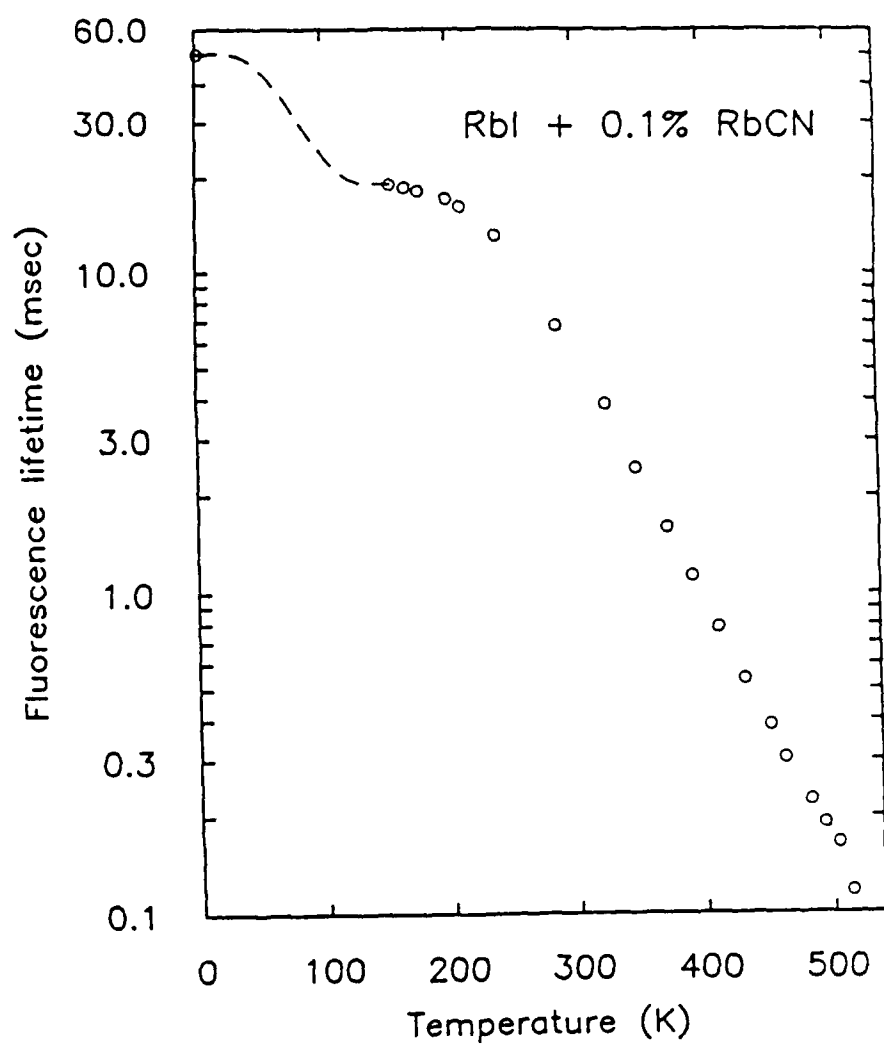
Figure 3. Lifetime versus temperature for a RbI host with a low
temperature point included. Dashed line shows the interpolated
temperature ~ ~pendence in the unexplored region.

### 2.2.3 Low temperature fluorescence measurements

#### cw fluorescence spectra

At temperatures below about 30 K, the broad emission spectrum from $CN^-$ observed at high temperatures begins to break up into a line spectrum as illustrated with trace (b) in Fig. (1). By combining a tunable diode laser pump together with a FTIR spectrometer the cw emission spectrum can be monitored over a broad frequency region at extremely high resolution. The total radiated power is greatly increased at low temperature due to the decreased nonradiative relaxation rate and the increased absorption of pump energy as the $CN^-$ linewidth narrows upon sample cooling. Figure (4) shows the emission intensity at 1.7 K for KBr, KI, RbI host crystals doped with 0.5 % isotopically pure $CN^-$ in the top three traces and CsI doped with 0.1 % $CN^-$ in the bottom trace[39]. The appearance of the line spectra at low temperatures can be attributed to electric dipole mediated vibrational energy transfer from the laser excited $CN^-$ ions in the v = 1 state to neighboring $CN^-$ ions, which in general are in arbitrary excited states as a result of previous energy exchanges. This up the ladder cascade of vibrational energy competes with the downward radiative and nonradiative transitions.

The simplist description of this cascade process can be given in two steps. First, resonant transfer of energy via electric dipole coupling occurs between a singly-excited $CN^-$ ion and a ground state ion:

$$CN^-(1) + CN^-(0) \rightarrow CN^-(0) + CN^-(1). \tag{2}$$
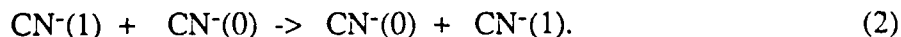
For the concentrations shown in Fig. (4) the hopping time between sites is estimated tobe ~ 2 μsec. The second step in the energy transfer process occurs when a pair of the highly mobile v = 1 excitations reside on a pair of nearest neighbor $CN^-$ molecules. If the two molecules are sufficiently close together, the much less likely nonresonant exchange

$$CN^-(1) + CN^-(1) \rightarrow CN^-(0) + CN^-(2) + 25 \text{ cm}^{-1} \tag{3}$$
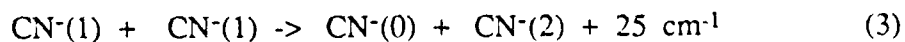
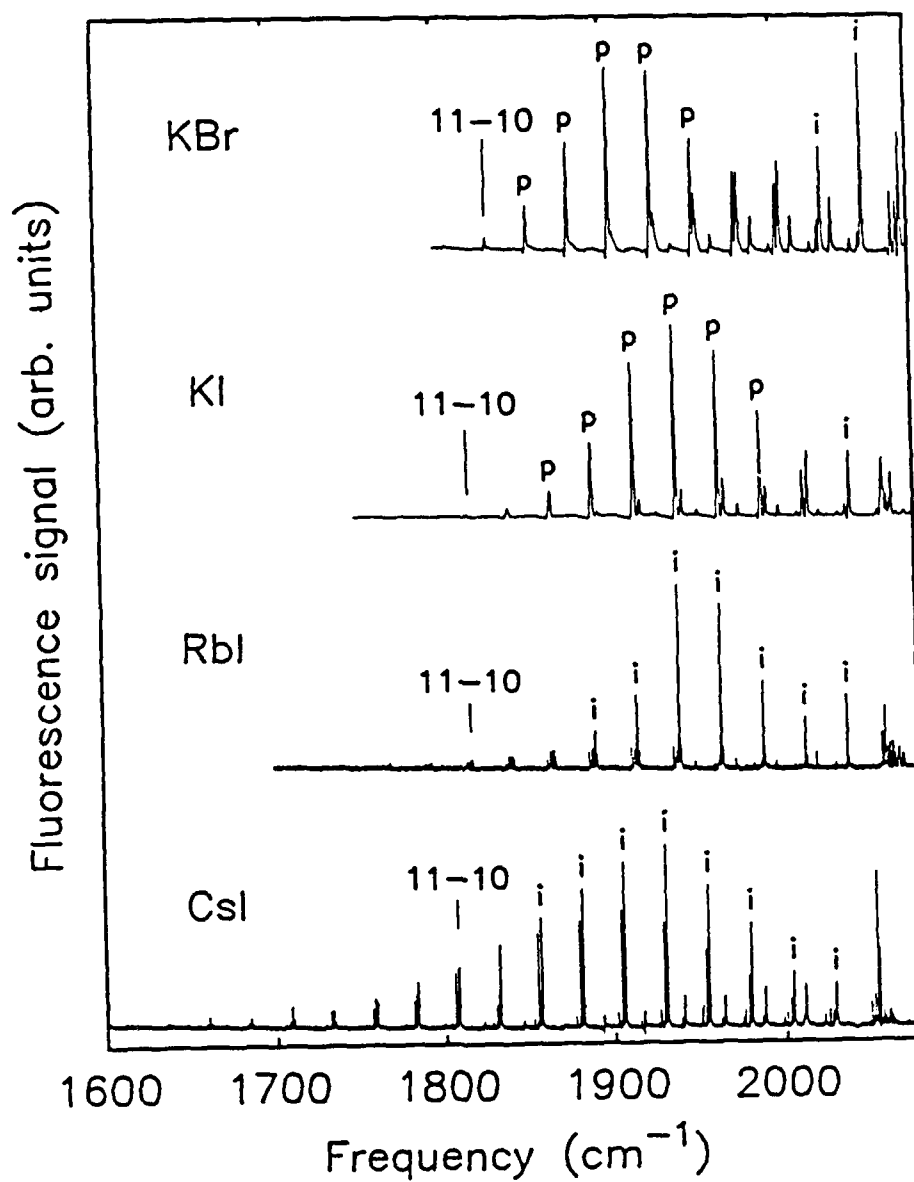can occur. This is due to the strong power law dependence of the resonant and

Figure 4. Broadband low temperature emission spectra from CN⁻ matrix isolated in a variety of alkali halide hosts. The $^{12}C^{14}N^-$ 10 -> 11 transition has been labelled for each host. The "i" label indicates transitions for isolated CN⁻ and the "p" label, for CN⁻ pairs. The sample temperature is 1.7 K.

nonresonant electric-dipole transfer probabilities, which for sufficiently small distance between molecules, favors up the ladder transfer over continued migration[39]. That the exchange given by Eq. (3) is a nonresonant process is due to the 25 cm$^{-1}$ mismatch between the 0 -> 1 and 1 -> 2 transitions which results from anharmonicity in the internuclear potential of the CN$^{-}$ molecule. The mismatch is compensated by the emission of one or more phonons.

It is important to note that when only electric-dipole interactions are responsible for energy transfer, migration of the $v = 2$ excitation by resonant hopping to the ground state ions is forbidden by the $\Delta v = 1$ dipole selection rule. On the other hand, the resonant exchange

$$CN^{-}(2) + CN^{-}(1) \rightarrow CN^{-}(1) + CN^{-}(2) \qquad (4)$$

which may follow from the approach of a mobile $v = 1$ excitation does lead to migration of the $v = 2$ excitation. Since the $v = 1$ population is generally much smaller than the $v = 0$ population, however, migration of the $v = 2$ excitations is certainly slow and probably negligible. The point to be made here is that since only the $v = 1$ population undergoes rapid migration, and since only very close encounters of $v = 1$ excitations with other molecules (in arbitrary energy states) results in nonresonant transfer, only singly-excited molecules may serve as energy donors. The general nonresonant exchange process may therefore be written

$$CN^{-}(1) + CN^{-}(v) \rightarrow CN^{-}(0) + CN^{-}(v+1) + \Delta E_v \, . \qquad (5)$$
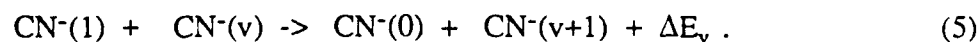
Here, $\Delta E_v = (E_1 - E_0) - (E_{v+1} - E_v)$ is the vibrational energy mismatch, which for cubic and quartic anharmonicity can be expressed succinctly as

$$\Delta E_v = v \, \Delta E_1 \, , \qquad (6)$$

with $\Delta E_1 = 25$ cm$^{-1}$ for CN$^{-}$.

In accord with the $\Delta v = 1$ selection rule for radiative vibrational transitions, the above considerations predict a sequence of emission lines spaced by 25 cm$^{-1}$ beginning with the

1 -> 0 transition at the pump frequency and extending to lower frequencies. This general behavior can be seen in Fig. (4). In addition, since the strength of a spectral emission line is proportional to the population difference between the two levels then population inversion occurs for those lines where the strengths in the sequence increase with decreasing frequency. All four traces show this effect for lines above $1950 \, cm^{-1}$.

Close inspection of the spectra in Fig. (4) show that in a number of cases the emission lines are doublets and that the population in one part of the doublet is different than in the other part. Careful concentration dependent flourescent studies have shown that the lower frequency component of each emission doublet is associated with pairs of $CN^-$ ions in the crystal[39]. The strongest emission component for each doublet in the figure is identified with an "i" for isolated molecule or a "p" for pair. Note that all spectra show a metamorphous in that the emission near the pump line is from isolated ions but the emission lines shifted the farthest to the red are associated with pair sites. The underlying efficiency of these pair complexes to accumulate a significant portion of the vibrational energy may stem from an unusual trapping mechanism. Within the pair one of the $CN^-$ molecules is always in the ground vibrational state ready to accept an excitation while the other neighboring molecule gets promoted to higher and higher vibrational levels with the capturing of each additional excitation.

A systematic study of V-V transfer has not yet been carried out at still higher dopant concentrations but because of the higher efficiency of $CN^-$ complexes to trap vibrational energy the result should be quite interesting with perhaps larger clusters stealing the vibrational energy from smaller ones. It should be noted that Lüty et al.[32], have varied the concentration of $CN^-$ in KCl and reported that "concentration quenching" eliminates most fluorescence by a concentration of 5% $CN^-$. Since an InSb detector was used to make this determination and since this detector does not operate at frequencies below 1900 $cm^{-1}$ inspection of Fig. (4) shows that at high concentration the emission peak may simply

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move to longer wavelengths beyond the detector window.

### temperature dependence

As the temperature is raised the line emission spectra of $CN^-$ in alkali halides is radically changed. In all cases vibrational energy is observed to travel farther up the anharmonic ladder so that the emission shifts farther to the red. A particular host lattice-dopant combination ($CsI + 0.1\% CN^- + 0.1\% Tl^+$) is illustrated in Fig. (5). [The $Tl^+$ ion does not play a role in this IR pumping scheme but it will be important later-Sec. 2.4- when the nonresonant UV pumping option is described.] At low temperature the emission output is peaked near 1900 $cm^{-1}$ and with increasing temperature a complex pattern appears with the center of gravity shifted to the red. The lowest frequency IR emission feature observed for this system at 23 K belongs to the 26 -> 25 vibrational transition in the ground electronic state of $CN^-$ pairs. This energy level is situated 5.2 eV above the ground state. At temperatures higher than about 30 K, the sharp line fluorescence disappears and extremely weak 1 -> 0 fluorescence is observed. The sloping background in the Figure is attributed to black body radiation.

### time-resolved fluorescence measurements

Considerably more information concerning energy transfer kinetics at low temperature can be obtained from time-resolved measurements of the multi-level vibrational fluorescence of the $CN^-$ ion. In addition to line strength information equivalent to the spectra previously presented, the time development of level populations can be directly observed and model calculations performed to more deeply investigate the microscopic transfer process. Some work has been carried out along this line with a grating monochromator but because the emission spectra are complex with frequency, time, concentration, temperature and impurity concentration describing five important variables, a systematic study of the time evolution of the emission has not yet been feasible and will depend on our ability to put together a time resolved FTIR spectrometer so that the Felgett
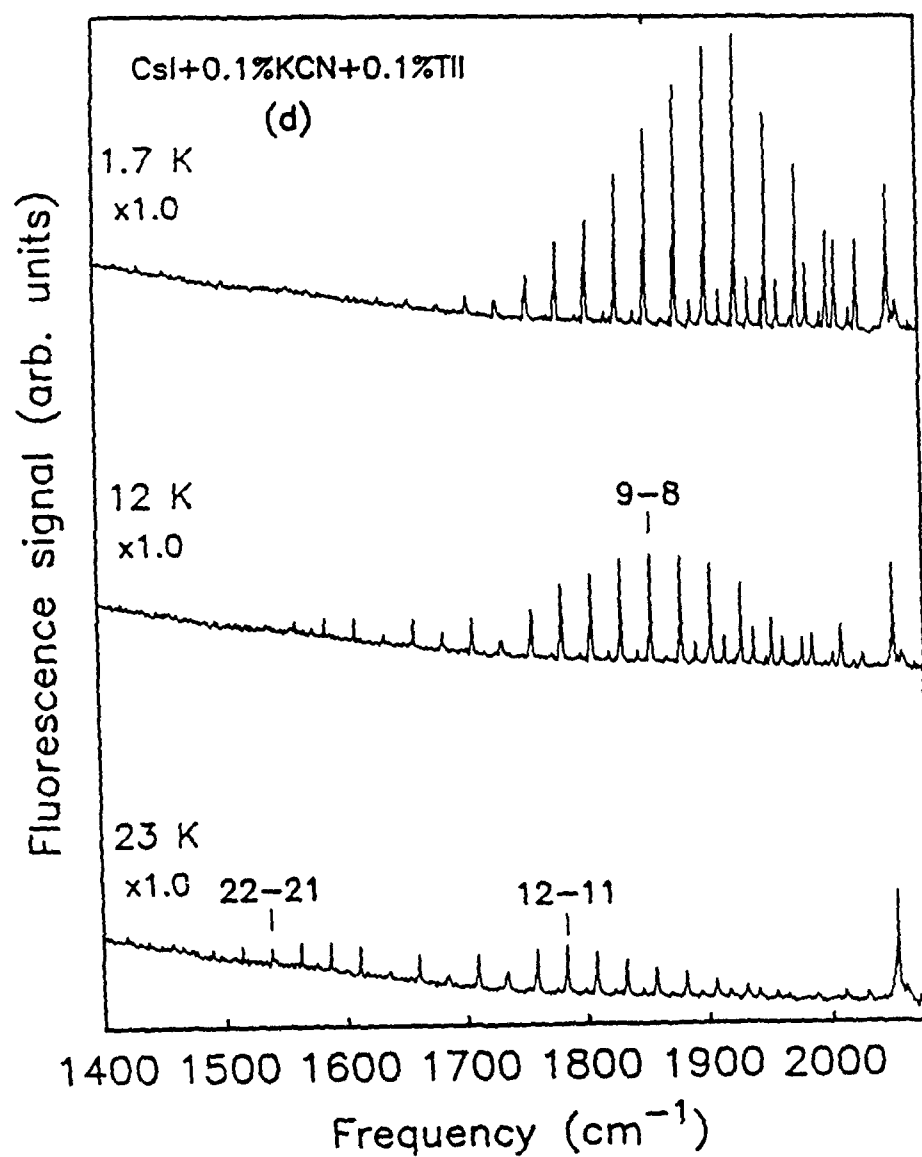
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Figure 5. Emission spectra for CsI + 0.1% KCN + 0.1 % TlI at several temperatures. the sharp line series disappears above T = 35 K.

advantage is recaptured.

Figure (6) shows the fluorescence intensity at 1.7 K for the first five vibrational transitions of CN⁻ for a KBr host doped with isotopically enriched KCN. As can be seen in the figure, rapid depletion of the $v = 1$ level resulting from energy transfer to other excited molecules yields an approximate 1 msec effective lifetime for the $v = 1$ state. Commensurate with the depletion of $v = 1$, the higher levels are rapidly filled.

## 2.3 The CN⁻ Doped Alkali Halide Laser

### 2.3.1 Experimental details

Optical pumping of alkali halide:CN⁻ lasers has been accomplished using three different laser systems for, fundamental, second harmonic and third harmonic vibrational transitions of CN⁻. For pulsed pumping of the fundamental, a frequency-doubled $CO_2$ TEA laser provides 100-ns, 500 μJ pulses at 4.8 μm at a repetition rate of 1 Hz. Continuous-wave or chopped pumping of the second harmonic at 2.4 μm is accomplished with a $KCl:Li(F_2^+)_A$ color center laser and cw pumping of the third harmonic of CN⁻ at 1.6 μm is accomplished with a $NaCl:F_2^+:O^{-2}$ color-center laser. The output powers of these lasers are approximately 50 mW and 1W respectively. All three systems yield linewidths of approximately 1 GHz.

Laser cavities are fabricated in two ways: the simplist technique is to evaporate mirrors and output couplers directly onto 1-mm² end surfaces of cleaved crystals ranging in length from 5 to 15 mm. End reflectors consist of 2000 A gold films with 100-μm to 300-μm holes masked off during the evaporation procedure, or $\lambda/4$ (3000-A) germanium films which provide approximately 30 % output coupling at the laser wavelength of 4.9 μm. In some instances, input coupling holes for laser pumping through the end reflectors also have beenused. The cavity lengths and KCN concentrations of these lasers are dictated by the optical pumping technique: Pumping of the weak overtone transitions generally
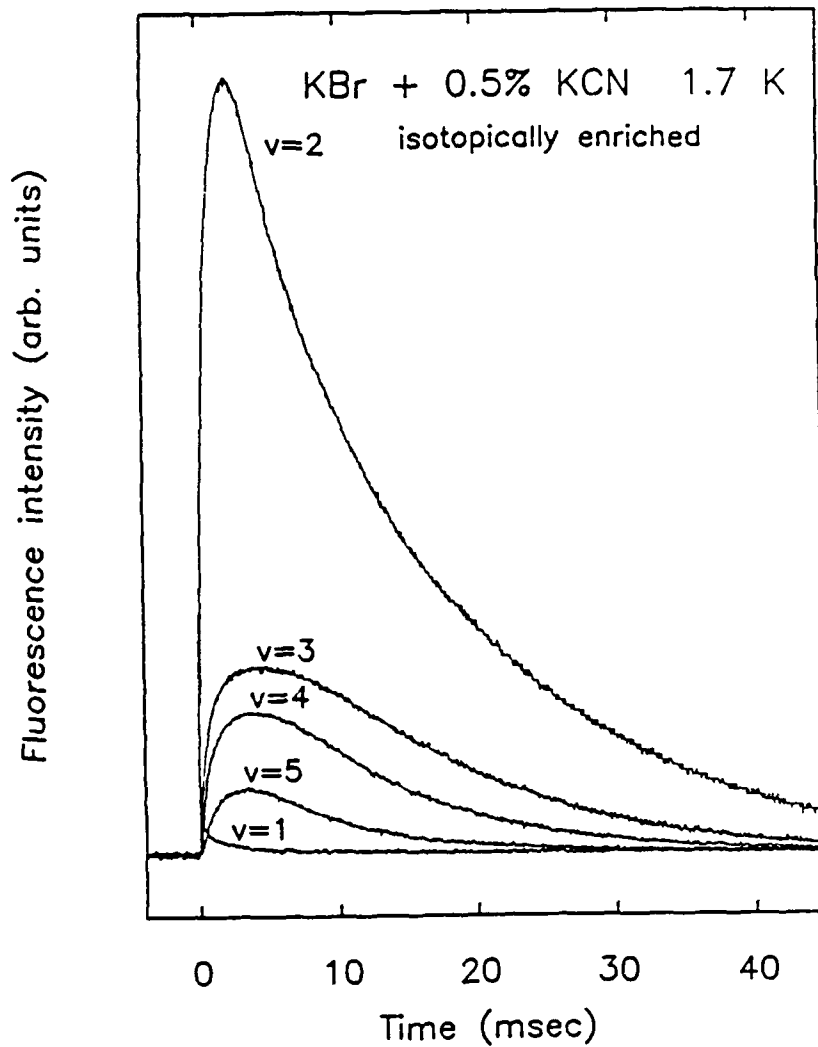
Figure 6. Time resolved fluorescence signals at 1.7 K from the first five vibrational transitions of CN⁻ in KBr + 0.5 % isotopically enriched KCN. The traces are labelled with the vibrational quantum number corresponding to the upper state of the appropriate transition.

requires longer cavities, higher concentrations, or both to insure efficient absorption of pump radiation. To exert more control over mode quality a more traditional optical resonator has been constructed around a cooled crystal using a flat end mirror internal to the cryostat and an external output coupler[37].

### 2.3.2 Experimental results on optical pumping

By optically pumping the fundamental, second harmonic, and third harmonic vibrational transitions of the $CN^-$ molecule, three different modes of operation have been tested. The second and third harmonic pumping configurations are particularly interesting because they demonstrate that the solid state molecular laser can be used to convert (with high efficiency) an IR pump input into subharmonic output radiation.

#### **first harmonic**

In the first type of these experiments[33], pulsed oscillation at 2054 $cm^{-1}$ was obtained on the 2->1 transition of CN- ions in a KBr host following pulsed optical pumping of the $CN^-$ $v=1$ lower laser level. Population inversion between the $v=2$ and $v=1$ levels subsequently arose in this system as a result of the phonon-assisted cross-relaxation (V-V transfer) process described earlier. The V-V transfer is sufficiently rapid and efficient at high impurity concentrations (0.05 to 0.5 mole%) that very little fluorescent emission is observed from the 1->0 transition. Gain coefficients as large as 1 $cm^{-1}$ were observed.

It is important to use isotopically pure dopant rather than naturally occurring KCN since a significant fraction of the initial pump energy is lost as a result of V-V transfer to the less abundant species $^{13}CN^-$ and $C^{15}N^-$ by the process

$$CN^-(1) + CN^-_{iso}(v) \rightarrow CN^-(0) + CN^-_{iso}(v+1) + \Delta E_{iso} . \qquad (7)$$

Here, $\Delta E_{iso}$ is the isotope shift, which is equal to 43 $cm^{-1}$ for the $^{13}CN^-$ species and 32 $cm^{-1}$ for the $C^{15}N^-$ species.

To my knowledge, the ability to obtain laser oscillation by optical pumping of the lower laser level followed by cross relaxation to produce population inversion is unique to the

alkali halide:CN⁻ system.

## second harmonic

More conventional laser pumping is possible due to the weakly dipole allowed overtone transition 0 -> 2 at 2.42 $\mu$m. Despite the factor of 100 weaker absorption in comparison to the fundamental, for samples doped at 0.5 % the measured absorption coefficient at the overtone is typically 2.5 cm$^{-1}$, so that a large fraction of the pump radiation can still be absorbed on a single pass through a 5-mm long gain medium[36]. With a KCl:Li(F$_2^+$)$_A$ color center laser , a population inversion between the 2 and 1 vibrational levels can be created. Only 26 $\mu$J is required to reach threshold when the upper laser level is pumped directly. This comparatively small threshold energy is a result of two facts: Firstly, a lower quantum efficiency exists in first harmonic pumping for conversion of pump photon into doubly excited CN⁻ ions owing to V-V transfer from singly-excited ions to ions in higher vibrational states. Secondly, a narrower gain bandwidth is produced by the 1-GHz linewidth of the color center pump laser in comparison with the 4.5 GHz gain bandwidth measured for the first harmonic pumping.

CW oscillation is also possible in this pumping scheme. This result is at first glance surprising, since normally only pulsed lasing is expected for a system in which the lower state lifetime is longer than the upper state lifetime. However the effective lifetime of the v = 1 level of CN⁻ is reduced to a value less than the upper level through the influence of V-V transfer processes, at least when the the v = 1 population is sufficiently large that these processes are important. Gain saturation of the 2 -> 1 transition creates such a large v = 1 population that the lifetime shortening effect of V-V transfer on this state is sufficient to permit cw oscillation on the 2 -> 1 transition. An interesting observation to make at this point is that in addition to inducing cw lasing, V-V transfer also adds to the laser efficiency by regeneration of the v = 2 population. Similar behavior has been observed by Prokhorov in an Er$^{3+}$- doped YAG laser[4].

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### third harmonic

For this experiment, a 15-mm$^2$ x 10 mm plane-parallel closed resonator was formed by evaporation of metallic silver films onto all faces of a sample of KI + 5% KCN[37]. Output coupling and pump beam injection was provided by a 0.5-mm diameter hole in the silver film on one of the 15-mm$^2$ faces. This approach was chosen over the open resonator configuration described above in order to favor trapping of pump radiation within the cavity ($\alpha < 0.01$ cm$^{-1}$ at 1.63 mm for 5% CN$^-$ concentration).

With the recent development of the high-power $F_2^+$:$O^{2-}$ color-center laser in NaCl (tuning range 1.55 $\mu$m to 1.65 $\mu$m)[43], the weakly allowed 0->3 transition of CN- at 1.63 $\mu$m (6,126 cm$^{-1}$) can be pumped. Figure 7 shows output waveforms obtained in response to an 18-ms 500-mW pump. Fig. 7(a) shows laser emission from the 3 -> 2 transition at 2017 cm$^{-1}$ superimposed on a fluorescence background. The laser output starts simultaneously with pumping of the 0 ->3 transition, but begins to terminate as the population builds up in the lower (v=2) level. Since the v=1 state has not been directly pumped, an inversion is soon established betweeen the v=2 and v=1 states. Figure 7(b) shows the near-simultaneous pulsed output at 2042 cm-1 from the 2 ->1 transition. The onset of lasing and subsequent saturation of the 2 ->1 transition is responsible for the secondary spike appearing on the output of the 3 ->2 transition, owing to the depopulation of the v=2 state.

It is worth noting that the above observation of "cascade lasing" and the already demonstrated significance of vibrational energy transfer processes in this solid-state context suggest an obvious analogy to the operation of CO gas lasers[44], a system in which exchange of vibrational energy among anharmonic oscillators is also important[45,46]. Since high power cw operation of the CO laser on high-lying vibrational levels (v=12 to v=18) is readily obtained at practical temperatures, a natural expectation is that high-concentration alkali-halide:CN$^-$ lasers might operate equally well under these conditions.
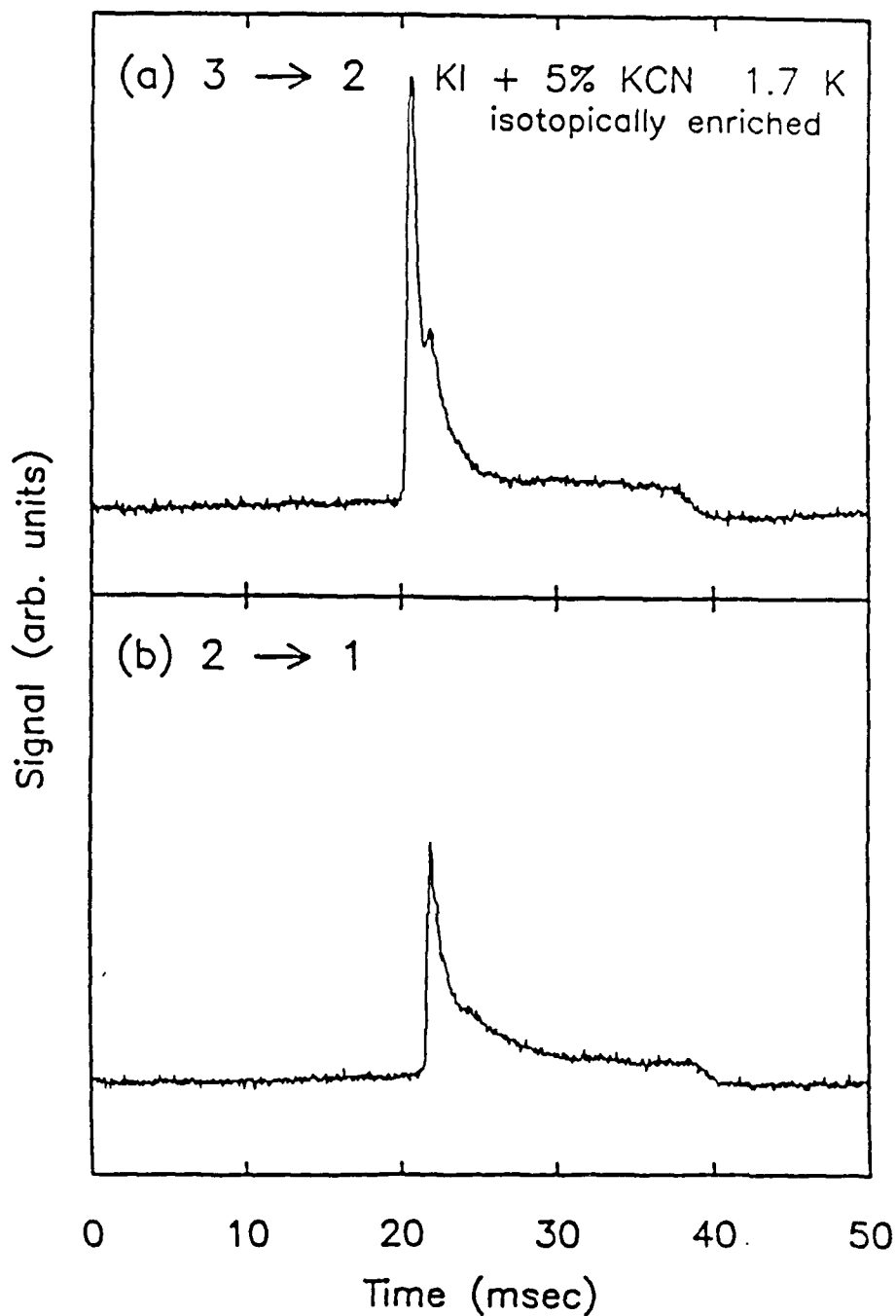
20

Figure 7. (a) Laser output at 2017 cm⁻¹ from the 3 -> 2 transition of
CN⁻ for a plane-parallel closed resonator. The laser is optically pumped
on the CN⁻ 0 -> 3 transition at 6,126 cm⁻¹.
(b) Output from the 2 -> 1 transition at 2042 cm⁻¹ is also observed. Note
the coincidence of the onset of lasing in the 2 -> 1 signal with the small
secondary spike in the 3 -> 2 transition. Only pulsed oscillation is
observed in this system.

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In fact, in contrast to the gas phase problem, the solid-state case may offer an important advantage: The only effective receptors of vibrational energy in endothermic gain-supressing exchanges are ground-state CN- ions,they are the most abundant species, and possibly singly-excited ions,they are the only "mobile" species. This suggests that the rate of thermally activated transfer from high-lying to low-lying vibrational states should be less for matrix-isolated CN- than for gas phase CO since only the largest possible activation energies will apply. At least on these fundamental grounds, high temperature operation of high-concentration matrix-isolated CN- lasers may in fact be easier to obtain. On the other hand, the practical problem of achieving effective direct excitation of high-lying vibrational states in a solid-state environment remains to be understood. Gellerman et. al.[47], have obtained oscillation at 77 K from CsCl samples co-doped with F-centers and CN- ions at very low concentration where V-V transfer is not important. In this case vibrational excitation results from optical pumping of the color centers in their red absorption band, followed by electronic-to-vibrational energy transfer to associated CN- ions.

This report[47] of CN- v=4-state excitation by direct transfer from electronic states of F-centers gives encouragement that a mechanism for high-vibrational-state excitation is possible. The prospect for a high-power solid-state analogue of the CO laser by itself should provide additional motivation for continued work on molecular defects in crystals.

## 2.4 UV Nonresonant Pumping of the CN- Vibrational Manifold

We have discovered that a complex IR vibrational emission spectrum occurs when CN- doped crystals are pumped with nonresonant radiation in the ultraviolet part of the spectrum at 308 nm[41]. A Lambda Physik 101-MSC Excimer laser giving typically 200 mJ per 20ns pulse at the output was used as a pump in these experiments. The laser energy incident on the sample was 20-30 mJ per pulse. To insure that IR emission from the laser

did not reach the IR detector, the pump pulse was first sent through fused quartz before reaching the sample. The IR signal from the sample was collected at right angles to the pump beam, passing through ZnSe and NaCl windows before being imaged through a Jarrell-Ash 1/4 Meter monochromator onto an InSb Detector. A digital storage scope was used to average the fluorescent signal from 32 laser shots at each grating position. To get the integrated intensity spectra, the signal is integrated in time at each monochromator position.

Both the time dependence of the IR fluorescence and the integrated intensity from each of the vibrational emission lines are shown in Fig. (8) for RbI + 0.2 % KCN . The strong line shown at the top of Fig. (8) corresponds to the 2 -> 1 transition and clearly demonstrates that over a one pulse cycle there is much more population located in level 2 than in any other part of the vibrational ladder. The bottom trace illustrates that level 2 has a larger population than level 1 over the entire time that emission occurs. Even more important the figure demonstrates that this new UV pumping scheme fills the ground electronic-vibrational level 2 preferentially over level 1 without any V-V transfer mechanism since a growth curve for the filling of this level is not observed even at μsec time scales. This trace should be contrasted with those shown in Fig. (6) where after a direct IR pulse coincident with the 0 -> 1 transition, V-V transfer is essential to provide the population in level 2.

Since the excited CN⁻electronic states have energies larger than the valence-conduction band gap of the host, the doped alkali halide crystals are completely transparent in this wavelength region. Although we do not yet have sufficient experimental information to make a quantitative identification of the vibrational pumping mechanism, we have determined that the effect is linear in incident pump intensity and not produced by a nonlinear effect such as two photon absorption. The IR emission results are clean enough to indicate that a new solid state conversion process of UV to IR has been uncovered.

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RbI + 0.2%KCN (Isopure)
1.4K

Integrated Intensity (arb)

1.0

0.6

0.2

-0.2

1900    1950    2000    2050    2100

Frequency (cm−1)

Fluorescence Signal (arb)

300.0

240.0

180.0

120.0

60.0

0.0

B

C

A

A 1=)0

B 2=)1

C 3=)2
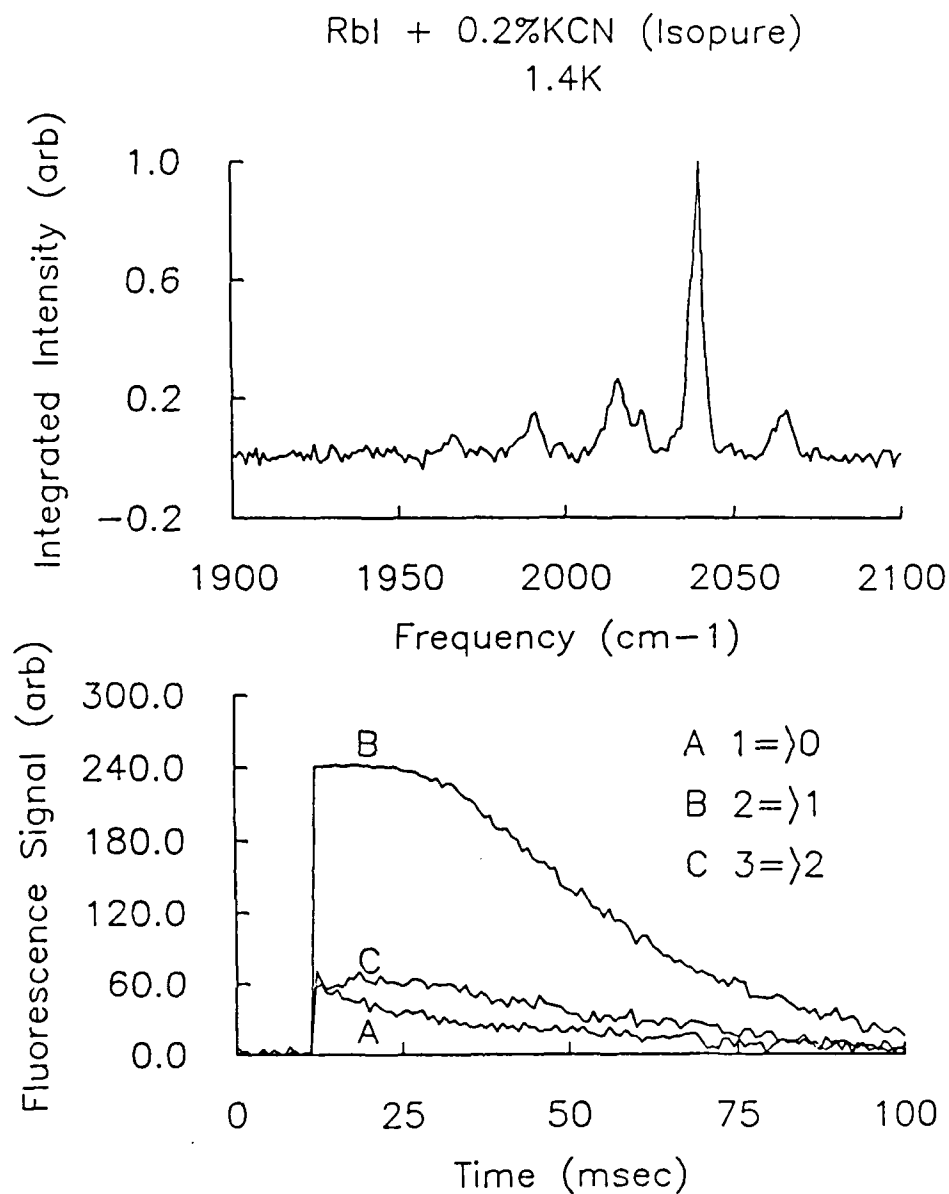
0    25    50    75    100

Time (msec)

Figure 8. Top graph: The frequency distribution of the integrated fluorescence intensity within the vibrational ladder.
bottom graph: Evolution of the fluorescence signal in time for three transitions. The 2 -> 1 signal much stronger than the 1 -> 0 demonstrates that population inversion has occurred. The UV pump sets up the initial distribution of vibrational population then the non-exponential dependence of the decay curves is produced by V-V transfer.

The initial energy transfer may stem from the creation of transient color centers in the laser radiation field made possible by the presence of a nearby molecular defect . We have found that the UV-IR transfer process is most efficient at elevated temperatures. In addition, the IR fluorescence from the de-excitation of the $CN^-$ vibrational manifold in the ground electronic state is observed to yield a series of anharmonically shifted transitions near 5 $\mu$m [see Fig. (8)] reminiscent of those spectra described earlier for directly IR pumped molecules. Exploratory measurements have shown that the strength of the IR emission grows with increasing host lattice constant and a shift in population to higher vibrational states occurs at higher pump intensities.

Figure (9) illustrates two of the new effects found with a RbI crystal double doped with $Tl^+$ and $CN^-$: (1) the metal ion impurity increases the total vibrational fluorescence output by an order of magnitude over that obtained from similar crystals which contain only the molecular impurity and (2) the spectral distribution in the anharmonic ladder depends on the UV pump intensity. The combined time and intensity dependence of this effect have not yet been measured.
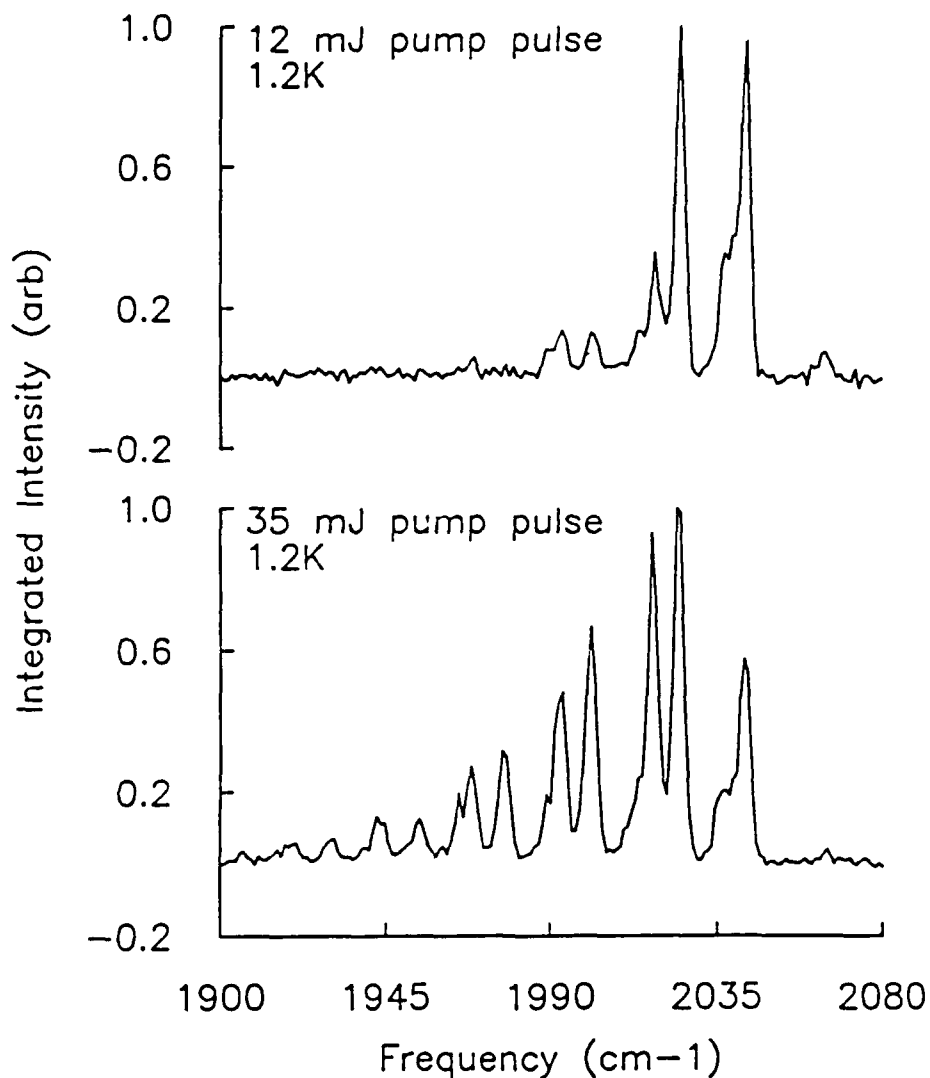
Figure 9. Pump energy dependence of the IR emission. In both cases population inversion occurs between the 2 -> 1 transition.The energy in the lower trace is a factor three larger than in the upper trace. The larger number of initially excited CN⁻ ions produced by the high energy pulse makes the V-V transfer mechanism more effective so the up the ladder cascade produces population inversion between 3 -> 2 as well as between 2 -> 1.

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